18
2-26-72

DR-2385 (2)

LA-5055

The Plutonium-Scandium System

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY JHKahn/amb
DATE 1/9/73

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

MASTER

R8205

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America. Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

LA-5055

UC-25

ISSUED: November 1972

The Plutonium-Scandium System

by

F. H. Ellinger
K. A. Johnson
C. C. Land

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

THE PLUTONIUM-SCANDIUM SYSTEM

by

F. H. Ellinger
K. A. Johnson
C. C. Land

ABSTRACT

The plutonium-scandium phase diagram was constructed from results obtained chiefly by x-ray diffraction and micrographic techniques. The principal features of the diagram were found to be as follows.

(1) There is a continuous series of solid solutions between the body-centered cubic phases ϵ Pu and β Sc.

(2) Face-centered cubic δ Pu is stabilized to room temperature by the solution of about 11 at. % Sc, and a maximum of 23 at. % Sc, decreasing to about 20 at. % at room temperature, is soluble in δ Pu.

(3) A maximum of about 47 at. % Pu, decreasing to about 25 at. % at room temperature, is soluble in hexagonal close-packed α Sc.

(4) A double-hexagonal, close-packed, intermediate phase, ζ , forms peritectoidally at 753°C and has a homogeneity range of about 34 to 41 at. % Sc at 663°C.

I. INTRODUCTION

Although the plutonium-scandium phase diagram presented here has appeared in a summary of plutonium phase diagrams,¹ the supporting data on which it is based have not been previously published. Because there are some discrepancies between this diagram and the versions published by Kutaitsev et al.² and Ballagny et al.,³ we consider it worthwhile to publish our experimental results belatedly.

II. EXPERIMENTAL

The plutonium metal stock was an electro-refined grade containing about 200 ppm by weight of impurities. The scandium metal stock was

supplied by the American Scandium Corporation, and contained about 0.5 wt % of yttrium as its main impurity. The alloys were prepared by arc melting on a copper hearth in a helium-argon atmosphere. The components for each melt (~ 5 g) were weighed to the nearest 0.1 mg, and, because melting losses were found to be negligible, we considered the intended compositions to be reliable and made no chemical analyses.

The alloy buttons to be heat treated were wrapped in tantalum foil and sealed in evacuated clear-silica capsules. The capsules were quenched in water without breaking. Thermal analyses were made in vacuo by the differential method, each alloy being sealed in a tantalum crucible having a

reentrant thermocouple well. The vacuum dilatometer was of the quartz-tube type employing a strain-gauge sensing element. The alloy samples, 1 in. long by 1/4 in. diam, were machined from castings.

X-ray-diffraction powder patterns were prepared using 114.59-mm-diam powder cameras with $\text{CuK}\alpha$ radiation. The samples consisted of unsieved filings sealed in evacuated clear-silica capillary tubes. The filings were stress-relieved and quenched while contained in the capillary tubes. We evaluated the lattice parameters of the cubic δ phase by graphical extrapolation using the Nelson-Riley function. We determined the lattice parameters of the hexagonal αSc phase by a computerized least-squares method.

The metallographic samples were prepared in a glovebox train having an air atmosphere. Polishing was done by standard techniques. Two etchants were used successfully: (1) 10 parts by volume of nitric acid, 90 water, and electrolytic ac and (2) 8 orthophosphoric acid, 5 glycol, 5 ethanol, and electrolytic dc. Microhardnesses were measured on a Leitz instrument using a 25-g load and a diamond pyramid indenter.

III. RESULTS AND DISCUSSION

The plutonium-scandium phase diagram shown in Fig. 1 has been constructed mainly from micrographic and x-ray-diffraction data. This system differs from those of plutonium with the rare-earth metals in that (1) the body-centered cubic allotropes ϵPu and βSc are mutually soluble in all proportions; (2) scandium dissolves much more extensively in δPu than do the rare earths, and it stabilizes the δ phase to room temperature; and (3) scandium forms an intermediate phase having a double-hexagonal close-packed structure.

A. Epsilon Plutonium-Beta Scandium Solid Solution

All alloy compositions solidify as the body-centered cubic solid solution that is continuous between ϵPu and βSc . We determined the solidus

Fig. 1. The plutonium-scandium phase diagram.

micrographically by examining quenched samples for evidence of incipient melting. The results are plotted in Fig. 1. Typical microstructures resulting from the decomposition of the $\epsilon\text{Pu}-\beta\text{Sc}$ solid solution on cooling to room temperature are illustrated in Figs. 2-4.

The $\epsilon/(\epsilon + \alpha\text{Sc})$ boundary was also determined micrographically. A typical microstructure that resulted from quenching from within the $\epsilon + \alpha\text{Sc}$ field is shown in Fig. 3. The massive grains of αSc are absent in alloys quenched from above the $\epsilon/(\epsilon + \alpha\text{Sc})$ boundary. The $\epsilon/(\epsilon + \delta)$ boundary was fixed by thermal-analysis data, and the $\epsilon/(\epsilon + \zeta)$ boundary was approximated by lattice-parameter measurements of the δ phase (transformed ϵ phase) in quenched $\epsilon + \zeta$ alloys. At 700°C, we found 18.6 ± 1.2 at. % Sc to be the maximum soluble in the ϵ phase.

Fig. 2. Plutonium-40 at.% scandium, arc-cast button, showing striated islands of δ , ζ , and α Sc phases in δ -phase matrix. dc 8-5-5 etch. 1000X.

Fig. 4. Plutonium-65 at.% scandium, treated at 1200°C for 10 min and oil quenched, showing the lamellar structure characteristic of transformed ϵ phase containing ~ 55 to 65 at.% Sc. ac nital etch. 500X.

B. Delta-Plutonium Solid Solution

Because preliminary work had revealed that the ζ phase was stabilized to room temperature by the solution of about 10 at.% Sc, and with lesser proportions could be retained at room temperature by quenching, we determined the δ -phase solvus by the x-ray parametric method. The lattice parameters of the fcc δ phase as a function of composition are listed in Table I and plotted in Fig. 5. The lattice parameters and corresponding

compositions of the saturated δ phase in two-phase 25- and 30-at.% Sc alloys equilibrated at a series of temperatures are given in Table II. These data indicate the maximum solubility of scandium in δ Pu to be 23 at.% at 663°C, which decreases to 19.9 at.% at 350°C, with apparently little further decrease at lower temperatures. The uncertainty in the solubility values is about ± 1 at.% Sc.

We determined the $\delta/(\delta+\gamma)$, $\delta/(\delta+\beta)$, and $\delta/(\delta+\alpha)$ boundaries by x-ray analyses of filings that contained 5, 7.5, and 10 at.% Sc and which had been treated at 250, 200, and 100°C for as long

Fig. 3. Plutonium-50 at.% scandium, treated at 932°C for 23 h and water quenched, showing grains of α Sc in a $\delta+\alpha$ Sc matrix (ϵ at 932°C). dc 8-5-5 etch. 500X.

TABLE I
DELTA-PHASE
LATTICE-PARAMETER/COMPOSITION
RELATIONSHIPS AND CALCULATED DENSITIES

Composition	Lattice Parameters ^a (Å)	Number of Samples	Calculated Density (g/cm ³)
5.0	4.6449±0.0004	3	15.20
7.5	4.6467±0.0004	4	14.86
10.0	4.6485±0.0007	15	14.52
12.5	4.6519±0.0006	6	14.17
15.0	4.6533±0.0006	10	13.84
17.5	4.6552±0.0006	4	13.50
20.0	4.6562±0.0006	12	13.23
22.5	4.6586±0.0004	7	12.83

^aUncertainty is the standard deviation.

Fig. 5. Delta-phase plutonium lattice parameter vs composition relationships.

as 10 months. The filings were originally taken from alloy buttons that had been homogenized in the δ region. The results are plotted in Fig. 1, and indicate that at least 11 at. % Sc in solution is necessary for thermodynamic stability of the δ phase at room temperature.

The $\delta/(\delta + \epsilon)$ boundary was placed by thermal data obtained with the 5- and 15 at. %-Sc alloys. The thermal results of the 15-at. %-Sc alloy were confirmed by dilatometry.

C. Alpha-Scandium Solid Solution

The maximum solubility of plutonium in hcp α Sc was found to be about 47 at. % at 753°C, the

TABLE II
LATTICE-PARAMETER DATA FOR THE
 δ -PHASE SOLVUS

Equilibration Temperature (°C)	Number of Samples	Mean Lattice Parameter (24°C, Å)	Solubility Limit from Fig. 2 (at. % Sc)
350	4	4.6568±0.0004	19.9
450	2	4.6571±0.0002	20.3
500	4	4.6576±0.0003	20.9
525	2	4.6574±0.0002	20.7
600	4	4.6579±0.0003	21.3
650	11	4.6588±0.0006	22.5

temperature of the ϵ Pu + α Sc $\rightleftharpoons$ ζ peritectoid reaction. As shown in Fig. 1, the solubility decreases with both increasing and decreasing temperatures. We located the limiting boundaries of the α Sc phase field by a combination of x-ray parametric and microstructural data, as indicated in Fig. 1.

The unit cell parameters of the α Sc solid solution are listed in Table III and plotted in Fig. 6. We used the "c" parameter to determine the composition of the saturated α Sc phase in the equilibrated two-phase alloys. These data are given in Table IV. The uncertainty in the solubility values is 1 to 2 at. %.

D. Zeta Phase

The sole intermediate phase of this alloy system was found to form peritectoidally at 753°C (DTA value) by the reaction of the ϵ solid solution containing 25 at. % Sc with α Sc having about 47 at. % Pu in solution. Microstructures typical of $\delta + \zeta$ and $\zeta + \alpha$ Sc equilibrated alloys are shown in Figs. 7 and 8, respectively. Zeta exists over a small homogeneity range. Volume-fraction (point-count) analyses of 30- and 35-at. % Sc-alloys that had been homogenized at 700°C for at least 500 h placed the plutonium-rich boundary of the ζ phase at about 36 at. % Sc. The scandium-rich boundary at 700°C was bracketed between 40 and 42 at. % Sc by means of microstructures.

The ζ phase crystallizes in a double-hexagonal, close-packed structure with $a = 3.3098 \pm 2$,

TABLE III
ALPHA SCANDIUM UNIT CELL PARAMETERS

Composition (at. % Pu)	a (Å)	c (Å)	c/a	Unit Cell Volume (Å ³)
0	3.3056±8	5.2666±24	1.5932	49.84
2.5	3.3101±7	5.2648±7	1.5905	49.95
5.0	3.3140±5	5.2626±8	1.5880	50.05
7.5	3.3160±4	5.2628±8	1.5871	50.11
10.0	3.3174±5	5.2611±7	1.5859	50.14
15.0	3.3209±9	5.2647±5	1.5853	50.28
20.0	3.3231±11	5.2720±18	1.5865	50.42
25.0	3.3249±5	5.2780±13	1.5874	50.53
30.0	3.3278±4	5.2902±6	1.5897	50.73
35.0	3.3276±9	5.2935±46	1.5908	50.76
40.0	3.3274±12	5.3113±25	1.5962	50.92

Fig. 6. Unit cell parameters vs composition of the hcp α -Sc solid solution.

$c = 10.7190 \pm 12 \text{ Å}$, and $c/a = 3.2386$ for the 40-at. %-Sc alloy. The calculated density is 10.54 g/cm^3 .

E. Microhardness Measurements

The ranges of diamond-pyramid hardness values (DPH, 25-g load) observed in the annealed phases are as follows.

Phase	DPH No.
δ	44-52
ζ	77-106
α -Sc	84-97

F. Atomic Volumes of the Phases

So that the average sizes of the atoms in the phases that are stable at room temperature may be compared, we have plotted the mean atomic volumes (volume of the unit cell divided by the number of atoms in the unit cell) as a function of composition in Fig. 9. Both terminal solid solutions deviate

Fig. 7. Plutonium-25 at. % scandium, treated at 650°C for 885 h and water quenched, showing ζ grains in a δ -phase matrix. ac nital etch. 500X.

positively from the Vegard rule. Because scandium exists only in the trivalent state, the size of the scandium atoms (all 12-coordination) probably remains unchanged in each phase. On this assumption, we calculated the volumes of the plutonium atoms as a function of the scandium concentration of the alloys, using the unit cell volumes and compositions.

These results are also shown in Fig. 9. It is shown that the plutonium atoms expand as their environment becomes increasingly rich in scandium atoms and that they reach a maximum volume

TABLE IV
LATTICE-PARAMETER VALUES OF THE α -Sc
SOLID SOLUTION IN TWO-PHASE ALLOYS

Alloy (at. % Sc)	Equilibration Heat Treatment		Lattice Parameters		Solubility Limit from "c" Parameter, Fig. 6 (at. % Pu)
	Temp. ($^\circ\text{C}$)	Time (h)	a (Å)	c (Å)	
55	800	142	--	--	
	+850	50	3.3276	5.3169	43.3
50	800	142	3.3266	5.3178	43.5
50	700	1177	3.3261	5.3195	44.6
50	650	1177	3.3272	5.3158	42.9
50	650	1177	--	--	
	+600	1271	3.3282	5.3082	39.5
60	600	1150	--	--	
	+400	6 mos.	3.3282	5.2918	32.4
65	800	192	--	--	
	+650	600	--	--	
	+400	10 mos.	3.3300	5.2936	33.2

Fig. 8. Plutonium-50 at. % scandium, treated at 700°C for 1177 h and water quenched, showing ζ phase (light) in an α -Sc solid-solution matrix. dc 8-5-5 etch. 500X.

Fig. 9. (a) Mean atomic volume vs composition. (b) Volume of the plutonium atom vs composition, assuming a constant volume for the scandium atom.

of about 26.22 Å^3 ($r = 1.667$) in the scandium-rich alloys. The increase in volume (or radius) corresponds to decreased valence of the plutonium atoms.⁴

ACKNOWLEDGMENTS

We wish to thank V. O. Struebing for making the alloys, P. Vigil for preparing the x-ray

specimens, and M. Gibbs for taking and measuring x-ray films. Helpful discussions with F. W. Schonfeld and W. H. Zachariasen are deeply appreciated.

REFERENCES

1. F. H. Ellinger, W. N. Miner, D. R. O'Boyle, and F. W. Schonfeld, "Constitution of Plutonium Alloys," Los Alamos Scientific Laboratory report LA-3870 (1968).
2. V. I. Kutaitsev, N. T. Chebotarev, I. G. Lebedev, M. A. Andrianov, V. N. Konev, and T. S. Menshikova, "Phase Diagrams of Plutonium with the Metals of Groups IIA, IVA, VIIIA, and IB," in Plutonium 1965, A. E. Kay and M. B. Waldron, Eds. (Chapman and Hall, London, 1967), pp. 420-449.
3. Alain Ballagny, René Boucher, and Claude Carrard, "The Pu-Sc System: Diagram and Properties," in Plutonium 1970 and Other Actinides, W. N. Miner, Ed. (The A.I.M.E. Metallurgical Society, New York 1970) pp. 699-706.
4. W. H. Zachariasen, "Crystal Structure Studies of Plutonium Metal," in The Metal Plutonium, A. S. Coffinberry and W. N. Miner, Eds. (The University of Chicago Press, Chicago, Illinois, 1961), Chap. 10, pp. 99-107.